Recovery of valuable metals from argon oxygen decarburization (AOD) dusts by leaching, filtration and solvent extraction

Virolainen Sami, Salmimies Riina, Hasan Mehdi, Häkkinen Antti, Sainio Tuomo

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12 # Recovery of valuable metals from argon oxygen decarburization (AOD) dusts by leaching, filtration and solvent extraction
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16 **Sami Virolainen, Riina Salmimies, Mehdi Hasan,**
17 **Antti Häkkinen, Tuomo Sainio**[*]
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20 *Lappeenranta University of Technology, Laboratory of Separation Technology,*
21 *P.O. Box 20, FI-53851 Lappeenranta, Finland*
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43 **Corresponding author. Tel.: +358 40 3578683, fax: +358 5 621 2350.*
44 *E-mail address: tuomo.sainio@lut.fi*
45

Abstract

For each ton of steel produced from a typical steelmaking plant, up to several tens of kilograms of dust, containing significant amounts of valuable and/or environmentally harmful metals, are also produced. A hydrometallurgical route for the recovery of these metals from argon oxygen decarburization (AOD) dusts, with selective leaching, filtration and solvent extraction was studied experimentally. Batch leaching of dusts with concentrated H_2SO_4 was found to be difficult to optimize for yields for the target metals (Zn and Mo), while keeping Fe in the solid phase. Zn and Mo could be recovered with comparable yields, while keeping Fe totally undissolved, by controlled leaching at pH above 3. Water was successfully used to leach Mo with 45% yield, while Ca, K, Cr, Mg, Pb, and Mn were leached as impurities. It was found that solid/liquid separation of the undissolved solids by pressure filtration was challenging and it was further observed that the properties of the initial dusts have a strong influence on this process step. D2EHPA was found to provide good extraction selectivity for Zn from acidic leaching solutions, except over Fe. A pure Mo/Cr mixture was extracted with hydroxyoxime LIX-84I, trioctylamine TOA and quaternary ammonium salt Aliquat 336. The best Mo/Cr selectivity was achieved with Aliquat 336.

Keywords

67 **1. Introduction**

68   In steelmaking, the amount of dust produced varies from roughly 15 to over 30

69 kg/ton of steel produced (Denton et al., 2005). Such dusts contain significant quantities of

70 metals, making landfill disposal more expensive or, even, impossible. In addition, valuable

71 resources are lost as the metals remain in the dust instead of being recovered. The

72 recycling of these dusts back into the steelmaking process would help to minimize waste

73 and improve material efficiency, but often they contain substances which lead to undesired

74 outcomes in the steelmaking process.

75   Dusts are formed through various mechanisms, for example volatilization of metals

76 and other chemical components and the mechanical formation of dust during gas blowing.

77 In addition, slag formers commonly contribute to dust formation during charging. The

78 composition of the dust varies, depending upon the amount of additives and on the raw

79 materials used (Jha et al., 2001). The characteristics and treatment of EAF (Electric Arc

80 Furnace) dusts have been reported more extensively than those for stainless steelmaking

81 dusts, generated by the AOD process (Argon Oxygen Decarburization).

82   In general, the main component in steelmaking dust is iron. Although the content of

83 zinc in EAF dusts is high, up to tens of percentages (Ruiz et al, 2007; Oustadakis et al.,

84 2010), in AOD converter dusts the fraction is usually below 10 wt.% (Neumeier and

85 Adam, 1986; Stefanova et al., 2013). Calcium, in turn, is present in large quantities in all

86 kinds of steelmaking dusts, as lime is commonly used in the refining process. The quantity

87 of Ca in the dusts often depends on the characteristics of the lime that is used. Other typical

88 metals in both EAF and AOD dusts include Cr, Mg, Mn, Ni, and Pb, whose concentrations

89 can vary between 0.01-10 wt.%, depending on the metal and on the steel grade being

90 manufactured (Havlik et al., 2012; Majuste and Mansur, 2008; Oustadakis et al., 2010;

91 Shinkai et al., 1997; Sofilić et al., 2004). Molybdenum has also been detected in several

92   dusts (Henderson and Roddis, 1998; Neumeier and Adam, 1986; Nogueron and Espi,,

93   1990; Shimakage et al., 1990, Stefanova et al. 2012).

94   Hydrometallurgical methods to treat the dust have certain advantages over

95   pyrometallurgical processes: (1) they are less energy-intensive and (2) dusts containing

96   relatively small quantities of valuables can be economically treated. In hydrometallurgical

97   processing, H_2SO_4 leaching has been reported to give somewhat higher yields for Zn from

98   EAF dust than HNO_3 or HCl (Shawabkeh, 2010). An exception is that in high

99   concentrations (> 2 M) the yields are better with HCl. Yields for Zn with H_2SO_4 are

100   usually around 70-80%, which is often acceptable, but the main disadvantage of H_2SO_4

101   leaching is poor selectivity over Fe, of which a significant fraction is also leached from

102   EAF dusts (Havlik et al., 2012, Shawabkeh, 2010). Based on the results of Shawabkeh

103   (2010) for EAF dusts, Zn/Fe selectivity is much better with HCl than it is with other acids,

104   as Majuste and Mansur (2009) also found for AOD dusts. Nevertheless, in practice, H_2SO_4

105   is usually used for acidic leaching.

106   The recovery of the valuable metals from the leach liquor first requires the separation

107   of this liquor from the solid residue. Filtration, in general, is one of the most commonly

108   applied separation techniques, but very few authors investigating the treatment of

109   steelmaking dusts have quantitatively considered this during initial feasibility studies.

110   Solid-liquid separation has been identified as a bottle neck in the hydrometallurgical

111   treatment of steelmaking dusts by several authors (Dreisinger et al., 1990; Eacott et al.,

112   1984; Frenay and Hissel, 1984; Youcai and Stanforth, 2000) but the published literature

113   mainly focuses on the qualitative, instead of quantitative, characteristics of this separation

114   step. The precipitation of iron oxides, and the further transformation of goethite into

115   hematite, has been suggested to improve filtration in some cases (Geutskens, 1990).

116   Pressure filtration, in general, is preferred over vacuum filtration when the particle size is

117 small, because of the high specific cake resistance, α_{av}, and limited differential pressure

118 achieved in vacuum filtration (Townsend, 2003).

119   Various separation and recovery methods have been used in hydrometallurgical EAF

120 dust treatment processes after leaching, including cementation of heavy metals with Zn

121 powder (Ruiz et al., 2007), selective precipitation usually with sulfides (Barrett and

122 Nenniger, 1992; Lenz and Martins, 2007; Tsakiridis et al., 2010; Youcai and Stanforth,

123 2000), Zn adsorption with ion exchange fibers (Kaneko et al., 1992), solvent extraction

124 (Barrett and Nenniger, 1992; Díaz et al., 2001; Lupi et al., 1999; Tsakiridis et al., 2010)

125 and electrowinning (Barrett and Nenniger, 1992; Lupi et al., 1999, 1999; Tsakiridis et al.,

126 2010; Youcai and Stanforth, 2000).

127   Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is the most widely used Zn extractant

128 for dust leaching solutions, due to its selectivity for Zn over many common metals and

129 high capacity (Díaz et al., 2001; Lupi et al., 1999; Tsakiridis et al., 2010). Bis(2,4,4-

130 trimethylpentyl) phosphinic acid (Cyanex 272) modified with tributyl phosphate (TBP) has

131 been reported to selectively extract Zn over Mn, Mg and Co from H_2SO_4 leachate of EAF

132 dust (Barrett and Nenniger, 1992). Asadi Zeydabadi et al. (1997) used hydroxyoximes

133 (LIX 622 and LIX 984) for selective Zn extraction, after the removal of Fe, Cd and Mn

134 from BF (blast furnace) dusts. 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (Kelex 100)

135 has been used to recover Pb prior to Zn extraction, but some Zn impurity was present in the

136 Pb stripping solution (Díaz et al., 2001).

137   Hydrometallurgical treatment to recover Mo has been reported less. Shimakage et al.

138 (1990) described a method in which the dust is leached with NaOH and Mo is precipitated

139 with H_2S. Also, leaching in water yielded good Mo recovery. Stefanova et al. (2012)

140 leached AOD dusts with NaOH at varying conditions and obtained high Zn and Mo

141 concentrations in the leach liquor.

142   To the best of our knowledge, solvent extraction has not been applied for the

143   recovery of Mo in the treatment of steelmaking dusts. In other cases a wide range of

144   extractant types (anionic, cationic, solvating) have been used because of the complex

145   aqueous chemistry of Mo. Examples of applicable reagents include Cyanex 272, bis(2-

146   ethylhexyl) phosphinic acid (PIA-8) (Zhang et al., 1995), hydroxyoximes LIX 63 (Zhang

147   et al., 1996), LIX 622 (Sastre et al., 2000) and LIX 84-I (Park et al., 2010), thiophosphinic

148   acids Cyanex 301 and Cyanex 302 (Saily et al., 1996), phosphinic acid Cyanex 600

149   (Söderström, 2010), tertiary amines (Alamine 336) and quaternary ammonium salts

150   (Aliquat 336) (Olazabal et al., 1992).

151   As references in the literature for AOD dust treatment are scarce and those for EAF

152   dust treatment abundant, the aim of this research was to develop, from a qualitative point

153   of view, a hydrometallurgical process to recover resources from two authentic AOD dusts

154   by applying similar methods to those that have been investigated for EAF dusts previously.

155   Recovery methods for Zn and Mo were of particular interest because of their economic

156   potential. The unit operations in the suggested process are selective leaching, filtration and

157   solvent extraction.

158   **2. Experimental**

159   *2.1. Reagents and analyses*

160   The AOD dust samples (referred to as AOD1 and AOD2) were provided by

161   Outokumpu Tornio Works (Finland). AOD1 is collected from the line in which

162   ferrochrome is fed as a melt and AOD2 from the line in which ferrochrome is fed in a solid

163   state. Chemical analyses of the dust were performed using XRF (X-ray Fluorescence), and

164   the results presented in Table 1. Detailed qualitative mineralogical analysis of the dusts is

165 presented in the article of Stefanova et al. (2013). The ZnO phase was present in both dusts

166 and, in addition, in AOD2 there was also a $ZnFe_2O_4$ phase. Mo was present as MoO_2.

167   The particle size distribution of the dusts was determined with a Beckman Coulter

168 LS 13320 laser diffraction particle size analyzer, using the Fraunhofer optical model for

169 the calculations. The particle size distribution of the AOD1 dust was found to be

170 multimodal with the median at 2.6 µm, d_{10} at 0.7 µm, and d_{90} at 13.5 µm. The distribution

171 for AOD2 was also multimodal and the corresponding values for the dust were 1.8, 0.8 and

172 17.3 µm, respectively. Here, the particle size distributions were based on volume fractions.

173   All of the chemicals used were of analytical grade, with the exception of the

174 kerosene diluent used for solvent extraction (Exxsol D80). The chemicals were supplied by

175 Sigma Aldrich, Fluka, Merck, and Exxon Mobil.   Metal analyses for leaching and

176 solvent extraction experiments were carried out from 10% HNO_3 media, using inductively

177 coupled plasma atomic emission spectroscopy (ICP-AES).

178 *2.2 Leaching*

179   Leaching experiments were performed in a 4 L glass reactor. Dust slurry with a

180 liquid to solid ratio of 5:1 (4 L/800 g in every experiment) was agitated at 170 rpm with an

181 anchor impeller (without baffles in the reactor) for 24 hours at 30 °C, while samples were

182 taken for metal analyses and pH monitored. Three different kinds of leaching experiments

183 were made:

184   1.   Leaching with pure water. This was made only with AOD2 dust.

185   2.   Direct leaching with 0.5 M H_2SO_4.

186   3.   Controlled leaching where pH was maintained close to, but above, 3.0 with

187   concentrated H_2SO_4.

188 *2.3 Filtration*

189   Solid/liquid separation of the leaching liquor and undissolved solid residue was

190   investigated only for the samples obtained from the H_2SO_4 leaching experiments. The

191   separation was performed with a laboratory scale Nutsche pressure filter using Pall T-1000

192   cellulose filter sheets with a filtration area of roughly 20 cm^2. All of the filtration

193   experiments were performed twice at 30 °C with 2, 3, 4, 5 and 6 bar pressure, generated

194   through pressurized nitrogen gas. The filtration pressure, as well as the mass of filtrate,

195   were recorded every 2 s during the experiments.

196   At the end of filtration, the cake thickness and mass were measured, and the cake

197   then dried at 105 °C for 24 h. The mass of the dry cake was measured afterwards, and from

198   this, the cake moisture calculated. TSS (Total Suspended Solids) and TDS (Total

199   Dissolved Solids) of the slurry were determined before and after the filtration test series by

200   filtering 100 mL of slurry with a laboratory scale Büchner unit and drying the cake and the

201   filtrate at 100 °C for 24 h. These analyses were done to verify that the characteristics of the

202   slurry had remained unchanged during the filtration test series, which took several hours.

203   The most important parameters that can be used for describing the filtration

204   characteristics of different suspensions are the average specific resistance, average porosity

205   and compressibility of the filter cake. According to the classical cake filtration theory

206   (Wakeman and Tarleton, 2005), the average specific cake resistance and medium

207   resistance for constant pressure filtration tests can be determined by plotting t/V against V.

208   The slope and the intercept of the resulting linear plot are used for determining the

209   resistances with the following equation:

210       $$\frac{t}{V} = \frac{\alpha_{av}\mu c}{2A^2 \Delta p}V + \frac{\mu R}{A \Delta p} \qquad (1)$$

211   Where t time, s

212	V	volume of filtrate, m^3
213	μ	dynamic viscosity of filtrate, Pas
214	c	filtration concentration, $kg_{solids}\ m^{-3}_{filtrate}$
215	α_{av}	average specific cake resistance, $m\ kg^{-1}$
216	A	filtration area, m^2
217	Δp	pressure difference, Pa
218	R_m	filter medium resistance, m^{-1}

219

220 The average porosity of a filter cake, ε_{av}, can be calculated from:

221
$$\varepsilon_{av} = \frac{V_{pores}}{V_{cake}} = 1 - \frac{V_{solids}}{V_{cake}} \qquad (2)$$

222 Where V refers to the volume of pores, the whole cake or the solid phase in the cake,

223 depending upon the suffix.

224 The compressibility of the filter cake describes the effect of pressure on the average

225 specific cake resistance or cake porosity. A convenient method for determining the

226 compressibility indices n and λ corresponding to cake resistance and porosity, respectively,

227 is to use the following equations:

228
$$\alpha_{av} = \alpha_0 \Delta p^n \qquad (3)$$

229
$$\varepsilon_{av} = \varepsilon_0 \Delta p^{-\lambda} \qquad (4)$$

230 Where α_0 and ε_0 are the average specific cake resistance and average porosity of a filter

231 cake, at unit applied pressure (Wakeman and Tarleton, 2005).

232   *2.4 Solvent extraction*

233   D2EHPA was chosen as the extractant for Zn recovery, since it is known to have

234   good selectivity. Solvent extraction isotherms were determined with 20 wt.% reagent

235   concentration in a 1 L glass reactor with O/A phase ratio 1:1, at 30 °C, with a mixing rate

236   of 1500 rpm. At the beginning of the experiment, the pH was adjusted close to zero with

237   concentrated H_2SO_4 and increased with ammonia gas during the experiment. Samples were

238   taken after the pH had not changed for 20 min. As aqueous phases, a synthetic solution and

239   a solution from direct 0.5 M H_2SO_4 leaching of AOD1 dust were used and compositions of

240   these solutions are given in Table 2. Cr was excluded from the synthetic solution but,

241   otherwise, the same metals were present in both solutions.

242   In order to study the selective recovery of Mo by solvent extraction, similar

243   experiments to those described above were made with four extractants at 0.5 M

244   concentration and 25 °C temperature. The extractants were LIX 84-I (BASF, active

245   component 2-hydroxy-5-nonylacetophenone oxime), Cyanex 301 (Cytec, bis(2,4,4-

246   trimethylpentyl)dithiophosphinic acid), TOA (Sigma–Aldrich, trioctylamine) and Aliquat

247   336 (Sigma–Aldrich, quaternary ammonium salt made by methylation of mixture of

248   trioctyl- and decyl amines). The leachate from the controlled pH leaching of AOD2 dust

249   was used as the aqueous phase for all four extractants. For TOA and Aliquat 336,

250   experiments were also performed using water leachate of AOD2 dust. In the latter

251   experiments, the initial pH was ~14, which was decreased gradually with concentrated

252   H_2SO_4.

253   In order to study the effect of extractant concentration on Mo selectivity, a series of

254   equilibrium experiments were made for each of the four extractants at 25 °C and a phase

255   ratio of 1:1. The reagent concentrations varied between 0.001 and 0.5 M. The controlled

256   pH leachate of AOD2 dust was used as the aqueous phase. The batches were equilibrated

257   for 20 min.

258   In all solvent extraction experiments, the extent of extraction, E_i, for each metal i was

259   calculated, based on the aqueous phase analysis, with the following equation:

260    $$E_i = \frac{c_i^0 - c_i^{eq}}{c_i^0}$$ (5)

261   Where c_i^0 is initial concentration of metal i and c_i^{eq} equilibrium concentration.

262

263   **3. Results and discussion**

264   *3.1 Characterization of dusts*

265   The composition of the dusts is given in Table 1; here, the compositional analysis

266   was used mainly to estimate the economic values of individual metals per kilogram of dust,

267   which are also given in Table 1. In AOD1 dust, the most valuable metals besides Fe are Cr

268   and Zn, and in AOD2, Mo, Ni and Cr.

269   *3.2 Leaching*

270   *3.2.1 Direct leaching with H_2SO_4*

271   Direct leaching of AOD1 dust with 0.5 M H_2SO_4 was found to occur rapidly (Fig. 1),

272   and no differences in leaching kinetics between metals were observed. The amounts of

273   leached metals did not change significantly from the first sample (15 min) until two hours.

274   Also pH increased rapidly at first: a value of 2.5 was reached within 15 min and a value of

275   2.9 only after two hours, indicating that most of the acid had been consumed at the

276 beginning (Fig. 1). However, pH increased continuously during the experiment (24 hours)

277 to 4.2, indicating that some reactions were still taking place, slowly. Concentrations for Zn

278 were 12.6, 13.4, 13.2 and 13.2 g/L after 15 min, 1 hour, 7 hours and 24 hours, respectively,

279 showing also that leaching was almost complete at 15 min and complete at one hour. The

280 yield of Zn at the end of the experiment was 67%.

281 The ongoing increase of pH caused back-precipitation of some leached metals such

282 as Fe and Cr (Fig. 1). This is beneficial, considering that the goal was to leave Fe in the

283 solid phase, but the pH increased slowly and the precipitation was not complete, even after

284 24 hours. In the final solution, concentrations of other significant metals besides Zn were:

285 Mg 2.0 g/L, K 1.4 g/L, Fe 1.0 g/L, Mn 1.0 g/L and Ca 540 mg/L. No Mo was leached in

286 this experiment and the yield for Ni was only 5.3% (c_{Ni} = 75 mg/L).

287 The AOD2 dust is more alkaline in nature, because of a higher CaO content than

288 AOD1 dust, which can be seen by comparing the direct leaching pH curves of the two

289 dusts (Fig. 1a and Fig. 2a). With AOD2, the pH increased gradually to 13.1 during the 24

290 hours of reaction, which caused back-precipitation of Zn, Ni, Mo, Mn and Mg. Fe was not

291 leached at all, since the pH increased immediately to 6.3. The highest concentrations for

292 Zn (2.8 g/L) and Ni (59 mg/L) were achieved after 15 min. For Mo, the highest

293 concentration (455 mg/L) was achieved after three hours of the experiment, when the pH

294 was 8.2. Corresponding yields were Zn 30%, Ni 1% and Mo 27%. After three hours, the

295 pH increased to 10.2, and Mo began to precipitate. Concentrations of other significant

296 compounds after 15 min were: Mg 1.9 g/L, K 1.0 g/L, Ca 540 mg/L, Mn 200 mg/L and Cr

297 150 mg/L.

298

299 *3.2.2 Controlled leaching at pH > 3*

300   As observed in Fig. 1b, controlled leaching of AOD1 dust was slower than direct

301   leaching. H_2SO_4 could be added only gradually, because of the need to avoid reducing the

302   pH to below 3.0, in order to prevent leaching of Fe. After one hour, when the pH had

303   decreased to 3.6, the system had reached a similar state as for direct leaching, but no Fe

304   had been leached. The concentration of Zn was 10.6 g/L at one hour and 10.9 g/L at 4.5

305   hours, indicating that leaching was complete after one hour. The Zn concentration was

306   somewhat smaller than with direct leaching and the corresponding yield for Zn was 55%.

307   Back-precipitation of Ca occurred to some extent, since it was leached rapidly when the

308   experiment was initiated (Fig. 1b). The pH at the end (4.5 hours) was 3.2 and

309   concentrations of other major compounds, besides Zn, were: Mg 1.6 g/L, K 980 mg/L, Ca

310   510 mg/L and Mn 270 mg/L. No Mo was leached in this experiment and the yield for Ni

311   was as low as 1.0% (c_{Ni} 15 mg/L).

312   The stronger alkalinity of AOD2 dust, compared to AOD1, was also observed in

313   controlled leaching: 147 mL of concentrated H_2SO_4 was consumed in AOD2 leaching,

314   compared to 77 mL in AOD1 leaching. The pH stayed at around 11.7 for 15 min before it

315   began to decrease (Fig. 1b). Also, with AOD2, the system reached a similar state to that at

316   the beginning of the direct leaching experiment, when the pH was lowered to 3.6. No Fe

317   was leached during the experiment and the concentrations of Zn were 2.6 g/L after two

318   hours and 3.2 g/L after 5.5 hours; the yield of Zn at 5.5 hours was 26 %. The yields for Zn,

319   with both leaching techniques, were significantly lower compared to AOD1 dust, which is

320   due to the fact that a proportion of the Zn occurs in AOD2 in the form of joint minerals

321   with Fe and cannot, therefore, be accessed without breaking this structure and also

322   leaching Fe.

323 After 5.5 hours, when the previously controlled reaction with AOD2 was left

324 overnight without controlling, the pH increased from 3.2 to 5.8, indicating that some

325 reactions still occurred, although Mo was the only metal that increased in concentration.

326 The concentration of Mo was the highest (1.1 g/L) in the beginning of the experiment,

327 when the pH was over 11 and the corresponding yield was 42%. When the pH started to

328 decrease, Mo started to back-precipitate, dropping the concentration to 270 mg/L. Some of

329 the Ca and Pb also precipitated back. In contrast, leaching of Ni started only when the pH

330 started decreasing, but the yield remained below 1%. Concentrations of other major

331 compounds, besides Zn and Mo, after 5.5 hours were: Mg 3.4 g/L, K 1.1 g/L, Ca 500

332 mg/L, Cr 230 mg/L and Mn 220 mg/L.

333 In both direct and controlled leaching, the type of dust was not found to affect the

334 leaching rate, except that lowering of pH in controlled leaching took more time with the

335 AOD2 dust, due its stronger alkaline nature. The high leaching rates are due to the small

336 particle size of the dusts (see Section 2.1). Considering the goal of this study, controlled

337 leaching was found to be a better option than direct leaching, since it enables a very high

338 Zn/Fe-selectivity to be achieved, without compromising the yield of Zn.

339 *3.2.3 Leaching with water*

340 Water leaching of AOD2 dust was at least as fast as acid leaching, though, naturally,

341 only some of the metals (Mo, Ca, Cr, K, Mn, Mg and Pb) were leached (Fig. 3). After one

342 minute, the concentrations of some metals had reached a maximum and the rest were

343 nearly at their maximum. The pH stabilized to 13.9, meaning that, actually, the leaching is

344 alkaline in nature. The maximum concentration of Mo was 1.2 g/L (yield 45%), but some

345 back-precipitation occurred after approximately 30 minutes. Nevertheless, water leaching

346 (or washing) of AOD2 dust seems to be a viable option to prepare a Mo-rich alkaline

347 solution free of major impurities such as Fe and Zn. Major compounds after 30 min were:

348 Ca 1.7 g/L, Mo 1.2 g/L, K 1.0 g/L, and Cr 140 mg/L.

349   Based on the leaching experiments and economic analysis (Table 1), Zn (AOD1) and

350 Mo (AOD2) were chosen as target metals for solvent extraction experiments.

351   To put the leaching results of the most relevant metals (Zn, Fe, Mo) into a theoretical

352 context, solubility curves were calculated using the MEDUSA computer program (KTH

353 Royal Institute of Technology, School of Chemical Engineering). Leaching curves of Zn

354 with the direct and controlled H_2SO_4 methods follow the theoretical solubility curve (Fig.

355 4). In the experiment with AOD1 (Fig. 1), the pH is below 4.2 meaning that all available

356 Zn is dissolved. With AOD2 (Fig. 2), Zn slightly precipitates back between pH ca. 6-8 and,

357 below that, the drop in solubility is abrupt. With the controlled leaching method the

358 concentration of Zn reaches its maximum almost immediately after the pH has dropped to

359 near 3.0 (Figs. 1 and 2). The highest achieved yield for Zn was only 67% (AOD1, direct

360 H_2SO_4 leaching), meaning that, since ZnO is easily dissolved inH_2SO_4 (Langová et al.,

361 2009), some of the Zn has to be located within the particles, so that it is not available for

362 the leachate. The Zn yields for AOD2 were lower than for AOD1, because it is partly

363 present as a $ZnFe_2O_4$ phase in AOD2. It is known that aggressive conditions are needed for

364 leaching Zn with high yields using H_2SO_4 from the $ZnFe_2O_4$ phase (Langová et al., 2009).

365   The direct H_2SO_4 leaching experiment with AOD1 was the only one in which some

366 Fe was leached (Fig. 1). This experiment was the only one in which the measured pH was

367 below 3.0 at any point, and the Fe started to precipitate back with the constantly increasing

368 pH. By leaching some of the Fe, part of the ZnO phase also becomes available to the

369 leachate, since with AOD1 the yield of Zn is higher with direct leaching than with

370 controlled leaching (67% vs. 55%). The behavior of Fe in every other experiment is also in

371 correspondence with the solubility curve (Fig. 4), so that none of the Fe is leached.

372   With Mo, the solubility plot (Fig. 4) does not totally explain its behavior in

373 controlled H_2SO_4 leaching. Some of the Mo precipitates back when the pH decreases from

374 8 to 3, although the solubility curve predicts that the precipitation would take place below

375 pH 3. Thus a predominance plot was constructed (Fig. 5), which reveals that precipitation

376 of MoO_2 takes place at higher pH than 3 when redox potential, Eh (SHE), decreases from

377 0.5 V.

378

379 *3.3 Filtration*

380   Average specific cake resistances and average cake porosities were determined for

381 each filtration test done with the two dusts and the results are summarized in Fig. 6. It can

382 be observed from the figure that the cake resistances were much higher for the AOD1 dust

383 than they were for the AOD2 dust. And, at the same time, the filter cakes produced from

384 AOD1 dust had significantly lower porosity than the cakes obtained from the AOD2 dust.

385 This means that the filtration rate of the AOD2-suspension is higher, but the final filter

386 cake also contains more liquid (48.0 +/- 3 wt.%) than the cake obtained from the AOD1-

387 suspension (31.5 +/- 2 wt.%)

388   As expected, decreased moisture contents and increased cake resistances were

389 observed with increasing pressure for both dusts. Increased compression of the cake results

390 in a decreased porosity which, in turn, results in a lower moisture content. The medium

391 resistance was roughly the same for all the experiments and it can also be noticed from Fig.

392 6 that the differences between the compressibility indices of the two dusts were negligible.

393 The different behavior of the two dusts is probably explained by the differences in their

394   particle size distributions and the surface properties of the particles. However, the particle

395   size distributions of the original dusts cannot be directly used, as the leaching stage prior to

396   filtration might affect the distribution. The original particle size distributions for the two

397   dusts did, however, show a difference between them. The particle size distributions for the

398   AOD1 and AOD2 dusts indicated that AOD2 was slightly coarser than AOD1, but that it

399   also had a wider particle size distribution. Even relatively small changes in the particle size

400   distribution can lead to increased or decreased average specific resistance of the filter cake

401   (Wakeman, 2007) which then leads to increased or decreased filtration time, respectively.

402

403   *3.4 Solvent extraction*

404   *3.4.1 Separation of zinc*

405   The selectivity order for D2EHPA with increasing pH is similar with both synthetic

406   and authentic (direct 0.5 M H_2SO_4 leaching) solutions: Fe, Zn, Ca, Mn, Mg, (Cr), Ni and K

407   (Fig. 7). This immediately shows the importance of selective leaching in the way that Fe

408   should be excluded from the solution coming to solvent extraction. If a solution containing

409   Fe was used for solvent extraction (for example if direct H_2SO_4 was chosen for leaching)

410   then Fe could be removed from the solution, for example by hydroxide precipitation. The

411   differences in $pH_{1/2}$ values of Fe and Zn are so small, 0.2 pH units for synthetic and 0.9 pH

412   units for authentic solutions, that it is not possible to first extract Fe selectively and then

413   increase pH for Zn extraction. Also, extraction of both Fe and Zn to D2EHPA and

414   subsequently stripping them out selectively is not a viable option, since Fe is known to be

415   difficult to strip having been extracted (Principe and Demopoulos, 2005; Sato et al., 1985).

416   In the authentic solution, the total amount of metals, and especially Zn, was high, which

417   moves extraction isotherms of the metals extracting after Zn towards a higher pH. This

418   implies that the concentration of D2EHPA should be selected carefully so that Zn is

419   extracted with a 100% yield, but also that there is not too much free extractant left for the

420   other metals. In this case the difference in $pH_{1/2}$ values of Zn and Ca was 2.0 pH units,

421   which is large enough for selective Zn extraction, but in the case of synthetic solution the

422   difference was only 0.5 pH units. It should be mentioned, however, that when there is no

423   Fe in the leaching solution, the extraction isotherms of other metals will move towards a

424   lower pH. As a conclusion, when the solvent extraction process is designed, isotherms with

425   different extractant concentrations should be constructed in order to choose an appropriate

426   one.

427   *3.4.2 Separation of molybdenum*

428   Four different solvent extraction reagents (LIX 84-I, Cyanex 301, TOA and Aliquat

429   336) were studied for selective recovery of Mo from controlled pH leachates of AOD2

430   dust. It was found that none had a pH region where they would extract only Mo (Fig. 8). In

431   many regions, sufficient selectivity was achieved over all metals except Cr. It should be

432   noted, however, that a Mo/Cr mixture could also be a potential end product for recycling

433   back to the steel making process. These regions are 0.0–4.0 for LIX 84-I, 0.0–2.5 for TOA

434   and 0.0–5.0 for Aliquat 336. Fe was also extracted in some of these regions, but the

435   amount of Fe initially in the aqueous phase was much lower (35 mg/L) compared to Mo

436   (513 mg/L) and Cr (218 mg/L), so this could be tolerated. With LIX 84-I between pH 0.0

437   and 1.5 the selectivity over also Fe is good.

438   For water leachate of AOD2 dust (Fig. 9) Mo/Cr product could be achieved in the pH

439   range 2.0-4.0 with TOA and in the whole studied range with Aliquat 336. The best Mo

440   selectivity over Cr was achieved with Aliquat 336 from water leachate when the pH was

441   0.7-2.2 (E_{Cr} = 16-34%). At pH 0.7 E_{Mo} was 97%, while 16, 7.1 and 0.8% of Cr, K and Ca

442   were extracted respectively.

443   The extraction behavior of the Cr and Mo is slightly different from controlled H_2SO_4

444   leachate and water leachate. There are two possible reasons for this: (1) The water leachate

445   does not have any sulfate at the beginning of the solvent extraction experiment, and thus

446   there are slightly different sulfate concentrations at similar pH points (2) There are more

447   metals in the controlled H_2SO_4 leachate, which affects the aqueous chemistry. Both of

448   these affect the amounts of the extractable anionic complexes.

449   Since the reagent concentrations in the pH isotherm experiments were high (0.5 M)

450   compared to the amount of metals (c_{tot} = 0.245 M), the effect of reagent concentration to

451   selectivity was studied between 0.001 and 0.1 M from controlled pH 3.0 leachate of AOD2

452   dust (Fig. 10). With LIX 84-I, Cyanex 301 or TOA the Mo extraction itself remained low,

453   mostly under 10%. With Aliquat 336, Cr was extracted completely at reagent

454   concentrations higher than 0.005 M. 72% of Mo was extracted with 0.005 M Aliquat 336,

455   from which the extent of extraction increased gradually to 100% at a 0.05 M reagent

456   concentration. It is thus concluded that high Mo/Cr –selectivity cannot be achieved using

457   the reagents studied,no matter what reagent concentration was chosen.

458

459   **4. Conclusions**

460   Based on the characterization of argon oxygen decarburization dusts in steelmaking,

461   possible target metals for recovery were found to be Zn (AOD1 dust), Mo (AOD2), Cr

462   (both) and Ni (AOD2). Selectivity in H_2SO_4 leaching over Fe was significantly improved

463   when the pH was controlled, by keeping it near to, but over, 3.0, while the yields for some

464   target metals (Zn, Mo) were not significantly lowered compared with direct H_2SO_4

465   leaching. Pure water was found to be both selective and fast as a leachate for Mo. With all

466   the studied leaching options, the process was very fast, due to the small particle size of the

467   dust. Based on the characterization of the leachates and economic analyses of the dusts, Zn

468   (AOD1) and Mo (AOD2) were chosen as target metals for the solvent extraction

469   experiments.

470   Filtration of the dust slurries was highly dependent on the material, giving the slurry

471   of AOD2 a better filtration performance in terms of filtration rate. The difference between

472   the porosities of the cakes obtained from the two dusts was significant and it showed that

473   the cakes obtained from AOD1 had a much denser structure and, consequently, also a

474   lower moisture content. An explanation for the different filtration behavior of the two dust

475   slurries could lie in their particle size distributions or in changes taking place during the

476   leaching process. If the underlying reason was the particle size distribution, flocculants and

477   coagulants could be considered in order to increase the particle size, at least in the case of

478   AOD1.

479   D2EHPA was found to be an effective extractant to recover pure Zn from an

480   authentic leachate of AOD1 dust. The selectivity can be improved by choosing the total

481   metal concentration to extractant concentration ratio so that there is no room for impurity

482   metals in the organic phase. Hydroxyoxime LIX-84I, TOA (trioctylamine) and the

483   quaternary ammonium salt Aliquat 336 were found to be suitable for obtaining a pure

484   Mo/Cr mixture. The best Mo/Cr selectivity was achieved with Aliquat 336 at pH 0.7,

485   where 97% and 16% of Mo (c_{Mo}^0 = 513 mg/L) and Cr (c_{Cr}^0 = 218 mg/L) were extracted,

486   respectively.

Acknowledgments

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595   Hydrometallurgy 41, 45–53.

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598
599 **Figure captions**

600

601 Figure 1. Leaching of AOD1 dust with a) 0.5 M H_2SO_4, and b) by keeping the pH close
602 to, but above, 3.0 with 96% H_2SO_4. L/S -ratio = 5:1 (L/kg), T = 30 °C. < 1
603 mg/L values have been converted to 1 mg/L for visualization.

604 Figure 2. Leaching of AOD2 dust with 0.5 M H_2SO_4 (a), and by keeping the pH close to,
605 but above, 3.0 with 96% H_2SO_4 (b). L/S -ratio = 5:1 (L/kg), T = 30 °C. Values
606 below 1 mg/L have been converted to 1 mg/L for better visualization on the
607 logarithmic scale.

608 Figure 3. Leaching AOD2 dust with water. L/S -ratio = 5:1 (L/kg), T = 30 °C. Values
609 below 1 mg/L have been converted to 1 mg/L for better visualization on the
610 logarithmic scale.

611 Figure 4. Solubility plots for Zn, Fe and Mo (Eh = 0.50). The plots have been calculated
612 using the MEDUSA computer program (KTH Royal Institute of Technology,
613 School of Chemical Engineering).

614 Figure 5. Predominance plot for Mo in sulfate solutions. The plot has been calculated
615 using the MEDUSA computer program (KTH Royal Institute of Technology,
616 School of Chemical Engineering).

617
618 Figure 6. Average specific cake resistances and porosities of the filter cakes obtained
619 from the leached AOD1- and AOD2-suspensions at different filtration
620 pressures.
621
622 Figure 7. Solvent extraction with D2EHPA from synthetic aqueous phase (a) and
623 solution obtained from 0.5 M H2SO4 leaching of AOD1 dust (b). T = 30 °C,
624 O/A = 1:1.
625

626 Figure 8. Effect of pH on solvent extraction of controlled pH 3.0 leachate of AOD2 dust
627 with 0.5 M (a) LIX 84-I, (b) Cyanex 301, (c) TOA and (d) Aliquat 336. T = 25
628 °C, O/A = 1:1.
629
630 Figure 9. Effect of pH on solvent extraction of water leachate of AOD2 dust with 0.5 M
631 (a) TOA and (b) Aliquat 336. T = 25 °C, O/A = 1:1.
632
633
634 Figure 10. Effect of reagent concentration on solvent extraction of controlled pH leachate
635 of AOD dust with (a) LIX 84-I, (b) Cyanex 301, (c) TOA and (d) Aliquat 336.
636 T = 25 °C, O/A = 1:1.
637